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THESIS

BONDING OF METALLIC SURFACES BY ADHESIVES

WILLIAM SANFORD HUMPHREY, JR.

1948

Thesis
H9

Postgraduate School
U. S. Naval Academy,
Annapolis, Md.

BONDING OF METALLIC SURFACES
BY ADHESIVES

A Thesis
Presented to the Faculty of the Graduate School
of Cornell University

For the Degree of
Master of Chemical Engineering

by
William Sanford Humphrey, Jr.
June 1948

BIOGRAPHY

William Sanford Humphrey, Jr. was born on August 17, 1919 in Osceola, Missouri. He graduated from high school at Tazewell, Tennessee in 1936, and joined the Navy immediately following graduation. He was appointed to the Naval Academy in 1939 by the Secretary of the Navy. While there he was active as a Company Commander and in athletics, winning letters in track, cross country and swimming. He graduated from the Naval Academy in June of 1942. During the war he saw action as a Motor Torpedo Boat Squadron Commander in the South and Southwest Pacific areas.

After the completion of the war he was selected for a three-year Naval postgraduate course in Chemical Engineering, the last two years of which were spent at Cornell University His major subject was Chemical Engineering and his minor subject was Administrative Engineering.

ACKNOWLEDGMENT

This work was undertaken at the suggestion of Dr. Charles C. Winding of the School of Chemical Engineering, and was carried out under his supervision. The writer wishes to express his appreciation to Dr. Winding for his inspiration and advice. The writer also wishes to express his appreciation to Professors C. W. Mason and A. Schultz of Cornell University.

Expressions of appreciation also go to Captain H. L. Dodson and Mr. D. Kallas of the Material Laboratory, New York Naval Shipyard, Brooklyn, New York.

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INTRODUCTION

The history of adhesives prior to the twentieth century deals largely with animal and fish glues which were used extensively as early as the Egyptian and Roman Renaissance. The development of casein and blood glues was a remarkable improvement over animal glues in the way of water resistance (46).

It is significant that adhesives were first introduced to this country by the furniture industry about the year 1808. Because these adhesives had very poor resistance to both moisture and fungus attack, they were regarded as inferior substitutes for other methods of assembly. Despite the inferiority of these adhesives, there was no great improvement in properties until the advent of synthetic resins just prior to World War II. The developments in adhesives during and since the war have been sensational.

Adhesive bonding, in its myriad forms, is today the most generally used method of joining materials. It has become as important an assembly method as welding, bolting, riveting, or soldering. A wide latitude in design features has been assured by highly developed bonding techniques that make it possible to join almost any two solids.

The adhesive industry, while not the most glamorous, is, nevertheless, a very essential industry. The synthetic adhesives represent one of the significant chemical developments of the past ten years, and have now progressed to the point of high production rates.

The adhesive industry is the third largest single user of resinous plastic materials, being exceeded only by protective coatings and molding-casting demands. The adhesive industry also accounts for approximately 60 per cent of the urea and melamine resins. In 1946, the monthly production of phenolic adhesives averaged 1,100,000 pounds and the urea and melamine adhesives, combined, averaged about 3,000,000 pounds (19, 33). The figures for 1947 represent a 13 per cent increase over 1946.

The acceptance of adhesives for stress carrying features of construction is clearly indicated

in present trends (6), such as in the fastening of automobile brake linings and as in general aircraft construction. Through the proper application of materials capable of meeting the performance requirements, adhesives will assume their proper place in the industrial picture. Already synthetic adhesives have registered a first by bridging the gap in metal-to-nonmetal bonding.

Much of this industrial progress has been empirical, rather than scientific development based on well-grounded theory, and progress is still being hindered by the lack of standardization and detailed information. Today the industry is ahead of research, and further new development must await the advance of fundamental investigation.

The present goal is an economically feasible adhesive for every application demand, easily formed and applied, that has physical properties at least as strong as the materials being bonded.

For a better understanding of the types of adhesives, a classified outline based on chemical origin is presented (4, 15, 31, 46).

Thermosetting Synthetic Resin Adhesives

Phenol-formaldehyde

Phenol-furfuraldehyde

Resorcinol-formaldehyde

Urea-formaldehyde

Melamine-formaldehyde

Furanes

Polyester resins (also alkyds and allyls)

Aniline-formaldehyde

Polyurethanes

Urea-resorcinol

Urea-melamine

Thermoplastic Synthetic Resin Adhesives

Polyisobutylene

Polyvinyl acetate

Polyvinyl chloride-acetate

Polyamides

Silicones

Polymethacrylic and polyacrylic esters

Coumarone-indenes

Polyvinyl butyral

P-Toluenesulphonamide-aldehydes

Polystyrene

Fatty acid resin

Polyvinyl ethers

Cellulose derivatives

Rubber and Synthetic Rubber Adhesives

Rubber latex

Natural or reclaimed rubber

Chlorinated rubber and rubber hydrochloride

Cyclized rubber

Polychloroprene

Butadiene-acrylo-nitrile copolymer

Synthetic resin-rubber combinations

Chlorinated synthetic rubbers

Cellulosic and Starch Derivatives

Cellulose nitrate

Cellulose acetate

Ethylcellulose

Methylcellulose

Sodium carboxymethyl cellulose

Starch, Dextrin

Natural Resins and Oils in Adhesives

Rosin and rosin esters

Shellac

Asphalts

Gum tragacanth

Ester gum

Linseed oil (oxidized)

Sulfite waste liquors

Water Soluble Gums in Adhesives

Gum arabic

Gum senegal

Cerasin gum

Protein Adhesives

Casein

Soybean protein

Zein

Adhesives of Animal or Fish Origin

Glue (hide, extracted bone, green bone)

Fish offal

Blood albumen

Soluble dried blood

Inorganic Adhesives

Sodium silicate

Portland cement

Magnesium oxychloride

Plaster of paris

Litharge-glycerin

Miscellaneous

Asphalt

Shellac

Oleo-resins

McBain and his British co-workers have done considerable pioneer work on the theory of adhesion, as well as on the development of test methods (29). This work has been closely paralleled and extended in this country by Browne and Traux at the United States Forest Products Laboratory. In more recent years the ASTM sub-committee on adhesives and the industrial research laboratories have carried on the investigation. Unfortunately much of the industrial research remains inaccessible in the secret files of the various companies.

During World War II, a number of investigations were undertaken; the objective being to develop a complete background of information on adhesives. The work done by the National Advisory Committee for Aeronautics during this period was a most valuable contribution to the technology of adhesives (37, 39).

THEORY OF ADHESION

Adhesion is defined as the state in which two surfaces are held together by interfacial forces (22). The theories of adhesion represent a series of complex phenomena that have long been controversial. Early investigators believed that adhesion depended upon mechanical strength obtained through solidification of the adhesive in the pores of the surfaces being bonded; they also suspected the presence of chemical forces. The present trend of thought is toward some form of specific adhesion. It is quite definite that the surface forces of the materials being bonded are in some respect involved in adhesion. The types of adhesion are now considered as mechanical, fusion, and specific with emphasis on specific adhesion (15).

It is possible that the characteristics of specific adhesion displayed by resins are due to the low molecular weight monomers or side-chains and that cohesive properties of the film formed are due to the higher molecular weight molecules. Thermosetting adhesives, when cured, have both small and large molecules.

Specific adhesion requires wetting of the surface not only by the solvent, but also by the ad-

hesive. Good wetting and evidence of chemical affinity are two of the properties which will indicate the probable behavior of the low molecular weight and unreacted monomers in normal resin adhesives (16, 39). Wettability is dependent upon various factors, including the viscosity of the liquid adhesive and its surface tension (45). The above is a hypothesis, and it is well to remember that the properties of specific adhesion are not clearly understood; it is known, however, that a surface inherits specific forces which can be modified by the absorption of either water or organic matter.

At least four types of bonding forces are important to adhesion; they are electrostatic, covalent, metallic, and Van der Waal's forces. Experimentally, these forces are extremely difficult to analyze; bonding energies have, however, been calculated by Pauling (35), and Leonard Jones (17) has established the electrostatic attractions that exist between surfaces and charged particles.

Many experts consider bonding as largely a function of surface chemistry (8, 13, 14). It is known that the surface of a solid can differ considerably from its internal structure (1, 21, 39). This is especially true of metals which have surfaces that are covered with oxide films, as well as adsorbed layers of gas. Struc-

tural changes may be initiated in a surface by the migration of active molecules into the surface layer and the adsorption of contact moisture or organic matter (45). It is true that various mechanical treatments, such as grinding, polishing, or abrading, may change the nature of the surface, but it is questionable as to how much this affects bonding. If metal is sublimed on a properly prepared surface, a crystal pattern is formed in the sublimed film. The surfaces of metals are crystalline in nature and consist of small blocks with a number of minute cracks, fissures, or grain boundaries of small dimensions. It is thought that the irregular structure at the surface results in non-homogeneous affinity for an adhesive. Experimental results, however, would indicate that this effect is not appreciable under normal conditions of surface preparation.

The Resinous Products and Chemical Company found that certain adhesives form stronger bonds with high valency metals than with low valency metals (39). This is substantiated by McBain's work (29). With different grades of steel the adhesion was poorest with silicon steels; perhaps due to the oxide film present.

It is not very clear just why cleanliness is so important to adhesion; it may be due to the reduction in wettability initiated by the contaminated surface, or it may be due to the reduction in the degree of polymer-

ization that results when the solvent disperses the contaminant among the monomers (3, 5).

It is considered that the following are important to adhesion: (2, 7, 30, 31, 34).

1. Surface tension of the adhesive.
2. Chemical nature of the surface.
3. Properties of the adhesive.
4. Thickness of the bonded film.
5. Method of application.
6. Solvents and solvent action.

The physical properties of adhesive bonds have been found to be related to the thickness of the adhesive film formed. It has been suggested that, if adhesive films were formed from 100 per cent liquid adhesive monomers containing no volatile solvent, the apparent strength of the assembly would be independent of the glue line thickness (8, 13). This has been partially substantiated by this experimental work since it was found, in the initial standardization, that film thickness is more critical when the total solids content is relatively low.

The present theories have not been found entirely applicable nor all-inclusive in this experimental work.

NEEDS FOR FURTHER INVESTIGATION

If the development in adhesives is to continue uninterrupted, and if industry is to meet the practical goals that are possible, basic research and development must continue at an accelerated pace. A complete literature review indicates the need for research in theoretical phenomena, in adhesive development, and in improved application techniques. Some of the specific problems influencing adhesion that warrant consideration are:

1. Surface chemistry.
2. Specific adhesion .
3. Standardization of synthetic types.
4. Methods of testing and appraisal.
5. Surface conditioning and wettability.
6. Use of solvents .
7. Thickness of glue line.
8. Adsorption of films on the solid surface.
9. Cleaning by heat treating (34).
10. Other cleaning methods.
11. Properties of adhesives such as viscosity, molecular structure, etc.
12. Low temperature catalytic adhesives.
13. Activated surfaces.
14. Effect of thermal shock on bond strength.

15. Effect of pressure and temperature.
16. Wetting power of adhesives and solvents.
17. Acidity or alkalinity of the adhesive.
18. Development of tapes and films for industrial application.
19. Low temperature strength properties of cured bonds.
20. Electro-deposition of synthetic adhesives on metals (23).

These are only a few of the many problems remaining to be adequately investigated if synthetic adhesives are to retain their rightful position in the field of structural bonding.

During the preliminary investigation involved in this work, it was decided first to explore the chemical and mechanical treatment of metal surfaces as related to bond strength. This pyramided into a general exploration as new problems were unraveled. This study was pursued as far as time and equipment permitted. The investigation was concluded by the development and testing of impregnated tissue films for metal-to-metal bonding.

Problems studied in this metal-to-metal bonding investigation:

1. The effect on tensile strength of the following variables:
    - A. Conditions of dry and precure of the adhesive prior to making the assembly.
    - B. Pressure functions during the cure period.
    - C. Mechanical surface treatment.
    - D. Chemical surface treatment.
    - E. Variation from metal to metal (steel, 2S aluminum, and 17 ST aluminum).
2. Adhesive carrier films of impregnated tissue paper.
3. Unsupported adhesive films presently in experimental pilot plant production.

STATISTICAL ANALYSIS

The execution of this experimental work necessitated the running of a large number of tests (some 500 specimens were tested), which consumed a considerable amount of time, although the minimum number of specimens was used for each test. This forced the use of a method of analysis that would give a measured degree of assurance with a minimum amount of data covering each variable that was studied. These circumstances justify the use of statistical analysis. The end point of this experimental work would be the successive elimination and determination of the variable, and can be arrived at, with some degree of assurance, only by the collection of considerably more data.

Statistical analysis is the application of scientific methods to:

(a) the control sampling of a body of numerical quantitative characteristics underlying the subject of inquiry,

(b) the condensation of the essential information to a few mathematical statistics which facilitate interpretation with a minimum of error,

(c) the formation of hypotheses regarding the true corresponding parameters and distri-

bution function of the universe of phenomena for which the datum is only a sample,

(d) the testing of these hypotheses in terms of sampling probabilities and their rejection or retention on the basis of qualified credibility,

(e) the redesign of old or the design of new experiments to gather data from which inferences may be drawn.

The fundamental basis of statistical analysis, and the one upon which the engineering statistician justifies its use in practice, is that useful knowledge is often empirical. This involves a concept of knowledge which includes three important components, (41), "(a) the data of experience in which the process of knowing begins, (b) the prediction P in terms of data that one would expect to get if he were to perform certain experiments in the future, and (c) the degree of belief p_b in the prediction P based on the original data or some summary thereof as evidence E".

There is much evidence in the literature of theoretical chemistry and physics to show that fundamental laws with which the engineer deals daily are statistical in nature. It may be easily demonstrated that such physical phenomena as temperature, pressure, viscosity, and entropy (from a molecular viewpoint) are in

essence statistical distributions. One might go on indefinitely, pointing out the statistical nature of such phenomena as the Brownian movement, Maxwell's distribution of molecular velocities, the density of a fluid, rates of diffusion and evaporation, rates of thermal and photochemical reactions, etc.

Controlled sampling is the very heart of statistical analysis, all inferences being objectively based on the original data. All quantitative data describing a physical or chemical event arises from the operation of one or more causes. It is usual that the number of causes producing any particular effect is extremely large. These causes, which cannot be identified and which are beyond comprehension, are termed chance or random causes. When only these causes are operating, when they are infinite in number and the variable is continuous, the statistical distribution is the normal curve. This distribution is generally utilized as the criterion of ultimate randomness.

Regardless of the type of measurements made, the data will vary according to some type of statistical distribution. That is, the measurements are subject to the influence of numerous unknown causes, and hence, with all measurements there is associated some type of error.

Statistical sampling procedures aim at a random set of observations. If a series is found to be non-homogeneous by test, it will be necessary to identify and remove these individuals of the series which are not compatible with the whole, or to remove those protuberant causes which are responsible for non-homogeneity.

These experimental data are interpreted through analysis of variance. This is contingent upon a normal distribution of specimens, and differentiates between variation due to chance and variation due to some significant variable (9, 10). Since no attempt is being made to derive relationships, correlation studies are not applicable. The derivation of the formulas used in analyzing the data are in the appendix, page 72. In a few instances the results are inconclusive by this method, and are so designated; in such cases the collection of more data is indicated.

EXPERIMENTAL WORK

DRYING AND PRECURE

Microscopical examination was used to study the nominal conditions for drying and precuring. First, various thicknesses of adhesive on the metal were studied. The thicker the film, the more difficult the problem of drying, and the more the cracks and blisters. This was determined by observing the drying of liquid adhesive film, 2, 4, 6, 8, 10, and 12 mils thick in a series of petri dishes. Once started, cracking proceeds very rapidly unless the rate of drying is reduced immediately. The starting points in the cracking or blistering function as weak spots in the surface destruction. Any pores or irregularities in a film act as weak spots where stresses develop and concentrate as activating forces. When the tensile strength in the vicinity of the weak spots is exceeded, cracks develop because of the oriented tension fields. Observed under polarized light, there were bright bands along the cracks and around the blisters, indicating internal elastic tensions. These increased in intensity as the cracks and blisters became more prominent.

If drying is too rapid, or the film is too thick, many blisters form. A reasonable explanation is that as the film dries too rapidly, a scum forms on the

surface, closing the pores and trapping the remaining solvent.

The forces of pull and pressure set up in the surface, when the film was too thick or the drying was too rapid, were quite obvious from the violent way in which the surface was distorted.

The precure must be such that polymerization is not extensive. If polymerization is carried too far, there is loss of strength at the adhesive-adhesive interface where the assembly is made.

Too rapid drying results in blisters and cracks. The heavier the film, the slower the drying must be; thus, a film just sufficiently thick to prevent a starved joint is the optimum. The optimum conditions were determined for each adhesive, and a low temperature dry was used to reduce blistering and to eliminate cracking.

It was found that a humid atmosphere during the drying period lowers the drying rate, and may result in unsatisfactory effects regardless of how well the other variables were controlled. This may be explained by the hygroscopic character of the solvent and the consequent absorption of water, not only at the surface, but throughout the adhesive body.

PRESSURE STUDIES

The effects of pressure were studied under the microscope, with the special arrangement pictured on pages 31-32, using two pyrex glass discs 5 inches in diameter and ½-inch thick. The pressure was applied through "C" clamps having steel reinforced cork jaws, and the temperature was regulated by the heated platens to be described in connection with the metallographic press.

One of the best illustrations of pressure effect (27) was found while investigating "Cycleweld 55-9", a phenolic-rubber base adhesive manufactured by the Chrysler Corporation. This adhesive, when examined in the partially polymerized state, and under the influence of heat and uneven pressure distribution, appeared to have inwardly oriented moleculles when viewed under polarized light. This would suggest either the presence of a peroxide catalyst or of hoop stresses. (See the photomicrographs on page 24.) When one of the pyrex plates cracked under pressure during the curing operation, this phenomenan was observed in the area immediately adjacent to the crack. It was possible to reproduce this phenomenan under any condition which gave uneven pressure distribution throughout the cure period.

Under normal pressure distribution there was polymerization and some flocculation, but no apparent

orientation. Steel specimens in which the uneven pressure distribution was evidenced in the failure, gave reduced tensile strength, thus indicating the importance of an evenly distributed pressure on the specimens during the cure.

In another experimental application the adhesive was applied to the pyrex discs and they were assembled. Heat was applied, and eventually gas bubbles formed (escaping solvent). Pressure was applied, and these solvent bubbles were forced to the edge and out from between the assembly. As polymerization continued, more bubbles formed and were unable to migrate to the edge because of the high viscosity. Pressure was increased and the gas bubbles were driven back into solution. Apparently the pressure increases the solubility of the gases in the fluid polymer, since the gases reappeared in bubble form when the pressure was released. This reversal was possible throughout the cure period as long as the adhesive was fluid.

Many contraction cavities were present in the various plates that were cured with little or no pressure. It is seen from the photomicrograph on page 25 that contraction cavities reduce the interfacial area between the adhesive and the surfaces being bonded; this impairs the total bond strength.

In still another experimental application, the pyrex discs were assembled, the liquid adhesive was degassed in a vacuum desiccator and flowed between the discs by capillary action; during the cure of this specimen there was no bubble formation and no evidence of gases being evolved.

This microscopical exploration would indicate that pressure in the curing of adhesive joints serves the following functions:

1. Insures flow of the adhesive to all parts of the joint.
2. Holds the mating surfaces in intimate contact.
3. Reduces the size and number of contraction cavities.
4. Reduces stress concentrations by insuring even pressure distribution.
5. Reduces the number of air bubbles in the cured glue line.

This study also indicated that vapor bubbles can be eliminated by the degassing of the liquid adhesive and the flowing of the adhesive between the mating surfaces by capillary action. This would require more investigation before industrial application could be recommended.

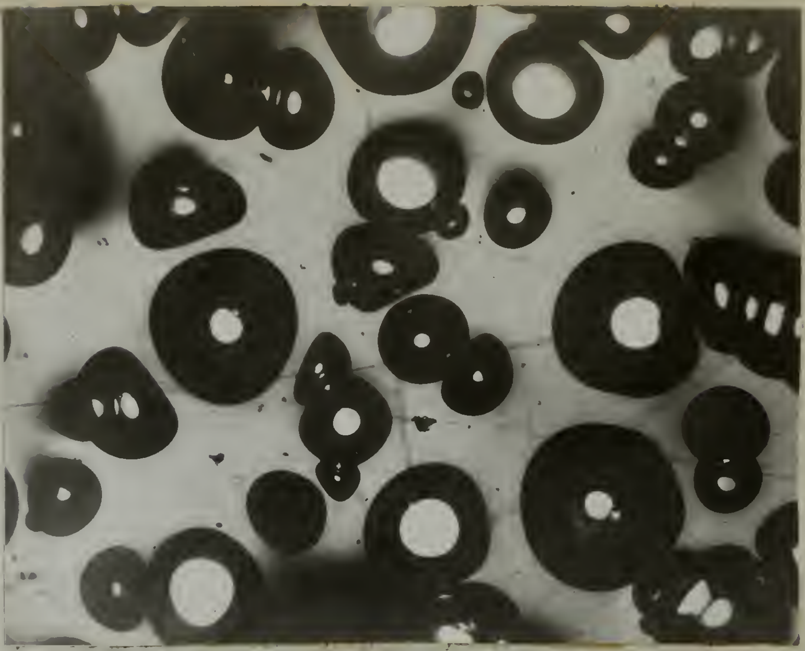


FIGURE 1

Cycleweld 55-9 with uneven pressure distribution.
(Photomicrograph - 90 X)

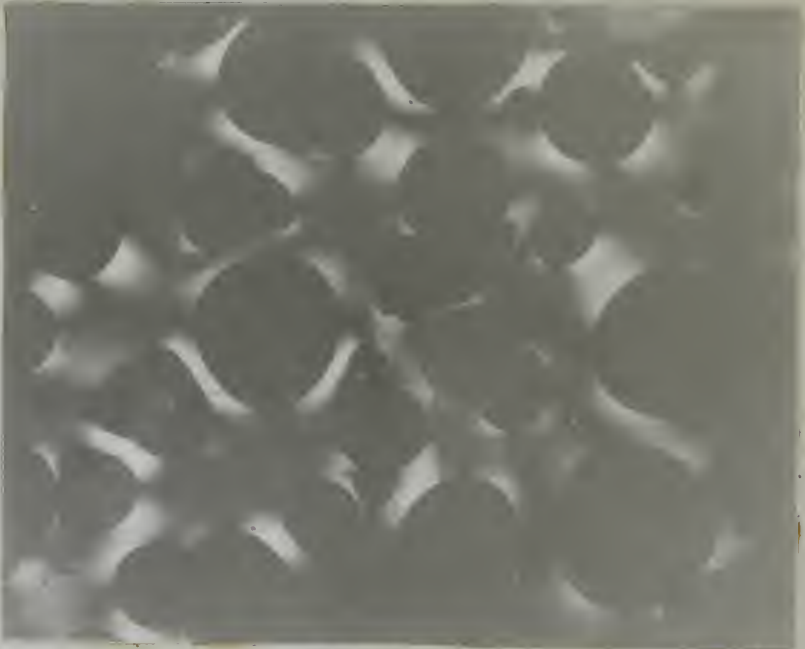


FIGURE 2

Same as Figure 1 with polarized light.

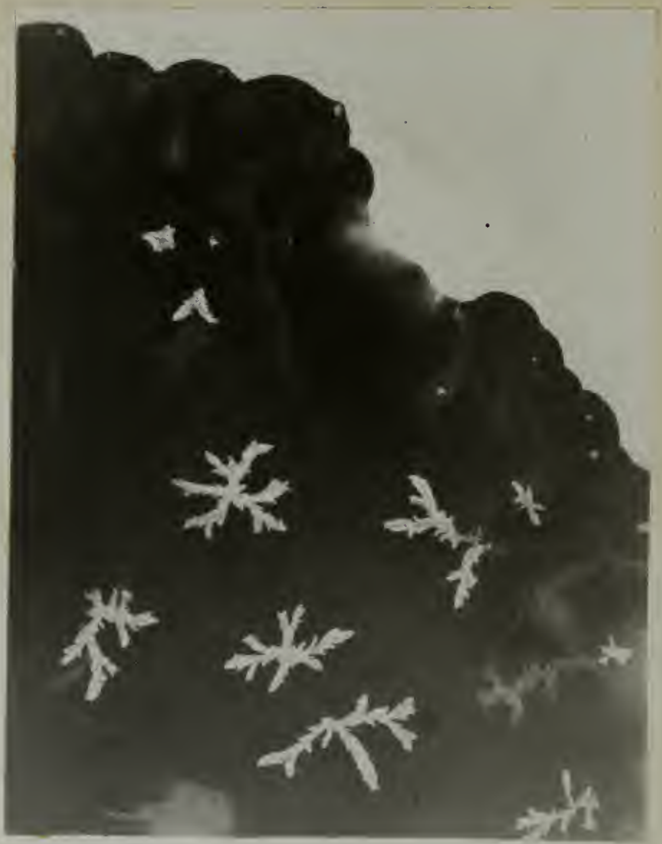


FIGURE 3

Contraction cavities with cycleweld 55-9.
(Microphotograph - 10 X)

SPECIFICATIONS

Some measures of bond strength is necessary in order to evaluate the various properties being reviewed. After a survey of the A.S.T.M. test methods, and the work of previous investigators, it was decided to adopt tensile testing as the primary method of analysis because it gives a better evaluation of bond properties than any other single test method presently in use, and because of the availability of equipment (23). During the standardization runs, which were made to determine the optimum conditions for bonding, the tensile testing was substantiated by double shear tests. Three types of metal specimens were used - mild steel, 17 ST aluminum, and 2 S aluminum; the selection was based on the availability of material and the desirability of correlating and extending previous work. Circular disc specimens, each having a bonding surface area of one square inch, were used for the tests. Round, rather than square, specimens were used in order to eliminate the point stresses at the corners of square specimens. Close attention was paid to the machining of all specimens.

The first data were concerned with the effect of mechanical surface treatment on bond strength. Specimens were tested under the following surface conditions: (11, 24)

1. Abraded - in an Olsen Wearometer for 100 revolutions, using aluminum oxide. This method of abrasion was selected because it gave reproducible results.
2. Metallographic polish - preliminary finishing at 250 r.p.m. on an Adolf G. Buleau finishing wheel down through triple zero paper. Final polishing was on a 1500 F - A B standard polishing head, complete with a 550 r.p.m. 8-inch balanced polishing disc. The polishing agent was a chromic oxide solution consisting of 30 grams of the powder and 10 cc of 5 per cent gum arabic added to one liter of distilled water.
3. As received - aluminum specimens had a history of mill finish; the steel specimens had a history of mill finish, followed by horizontal grinding to provide parallel faces.

To insure that no cleanliness variable was introduced, the same cleaning procedure was used for each series of tests. After many standardization trials, it was decided to use a solvent degrease following the surface preparation because of ease and speed of application (28). The degree of cleanliness was determined by the water break test. It is common knowledge that a clean metallic surface will support a continuous water

layer. If the water layer breaks and runs off irregularly, the surface requires more cleaning. Acetone was used as the degreasing agent.

APPLICATION OF ADHESIVE (42)

The film of adhesive was applied by dipping the prepared metal surface, as soon as it was clean and dry, into the liquid adhesive. The proper viscosity of the adhesive, to give the desired film thickness, was determined by standardization runs prior to actual dipping. This must be so regulated that the final cured glue line is between two and six mils in thickness which is the industrial practice. The combined drying and precuring time is 18 hours. Preliminary investigation revealed the presence of vapor bubbles in the uncured film; subsequent drying was accomplished in a vacuum desiccator. It is possible that this removal of air, vapor, and oxygen from the film may have introduced another variable; however, if such was the case, then the variable was present in all applications (13, 15). It is important that temperature control be employed during the precure period, and that the adhesive is not heated too rapidly; otherwise, the surface pores close quickly, trapping solvent, and leaving bubbles and contraction cavities in the cured bond. See Figure 3 on page 25.

CURING

A standard Fischer metallographic specimen press, which applies pressure hydraulically through two heated brass platens, was used for the curing operation. The platens are $4\frac{1}{2}$-inches square and 1-inch thick, each contain a thermometer well and two 150-watt rheostat-controlled finger heaters. A sheet of asbestos board separates each platen from the press. Standard shim stock was used to level the platens and to insure even pressure distribution. The press is ideally suited for the application.

The specimens were introduced to the press after the platens had reached curing temperature; a better procedure might have been to introduce the specimens with the platens at room temperature and gradually work up to curing temperature. However, time did not permit such a practice, and the results were consistent when using the procedure outlined.

The bonding procedure used was, in general, as follows:

1. Dip the prepared bonding surface of the clean and dry specimens into the liquid adhesive. It was found advantageous to keep the total solids content high in order to minimize solvent effect and bubble formation.

2. Drain the surface momentarily and set the disc in a horizontal position with the film surface upper-most.
3. Allow film to dry as instructed by the adhesive manufacturer. (Eighteen hours for Textolite.)
4. Maintain the platens at the curing temperature.
5. Introduce the assembled specimen into the press, being careful to maintain alignment of the specimen discs throughout the cure.
6. Apply optimum pressure and temperature for the optimum time.
7. Release pressure and remove specimens.
8. Cool specimens in the air and measure the glue line thickness. (Final glue line thickness must be in the range .002-.006 inches.)

From the standardization runs it was found that temperature, pressure, and time must be controlled throughout the cure period in order to insure reproducible results. It is necessary to determine experimentally the optimum conditions for each adhesive.

The temperature controls the rate of cure, and consequently, the time of cure. It was found that a slight change in temperature materially changes the strength of the bond.

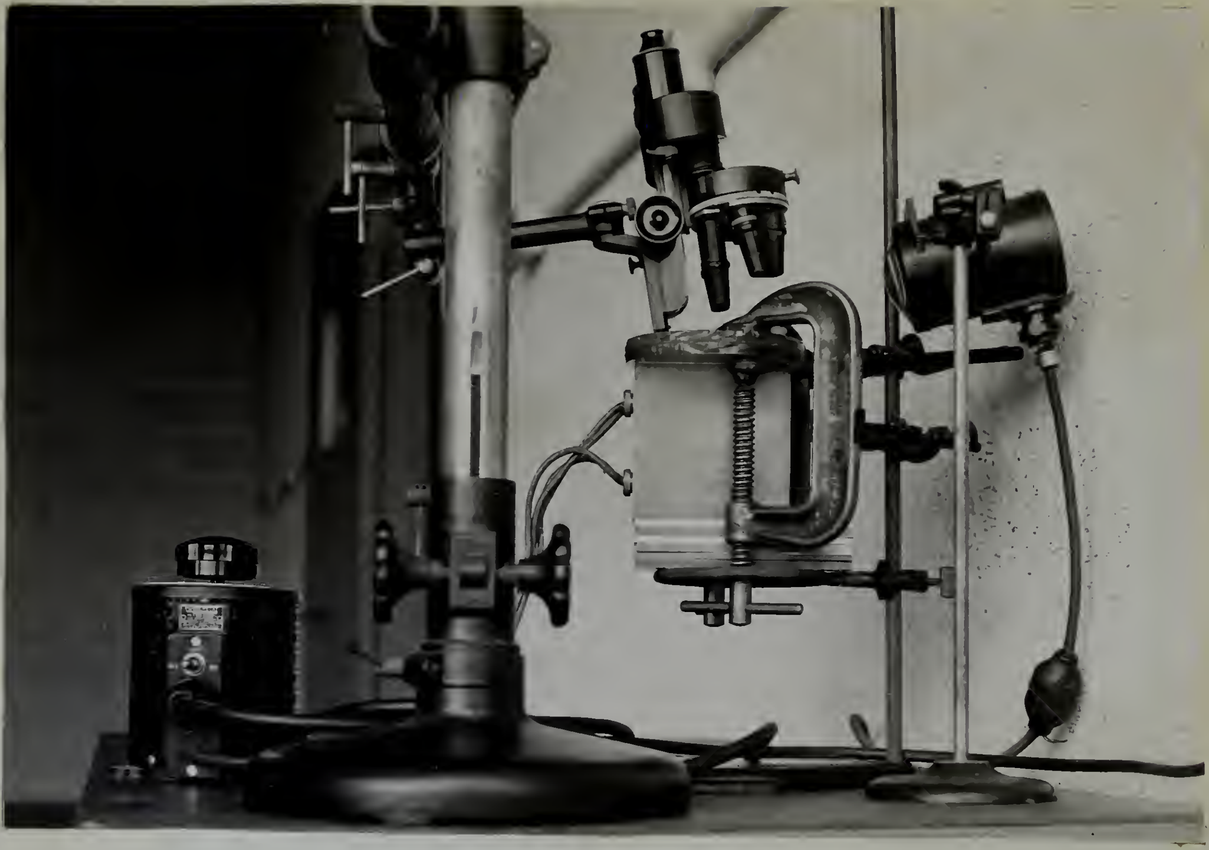


FIGURE 4

Apparatus used for Curing and Pressure Studies.

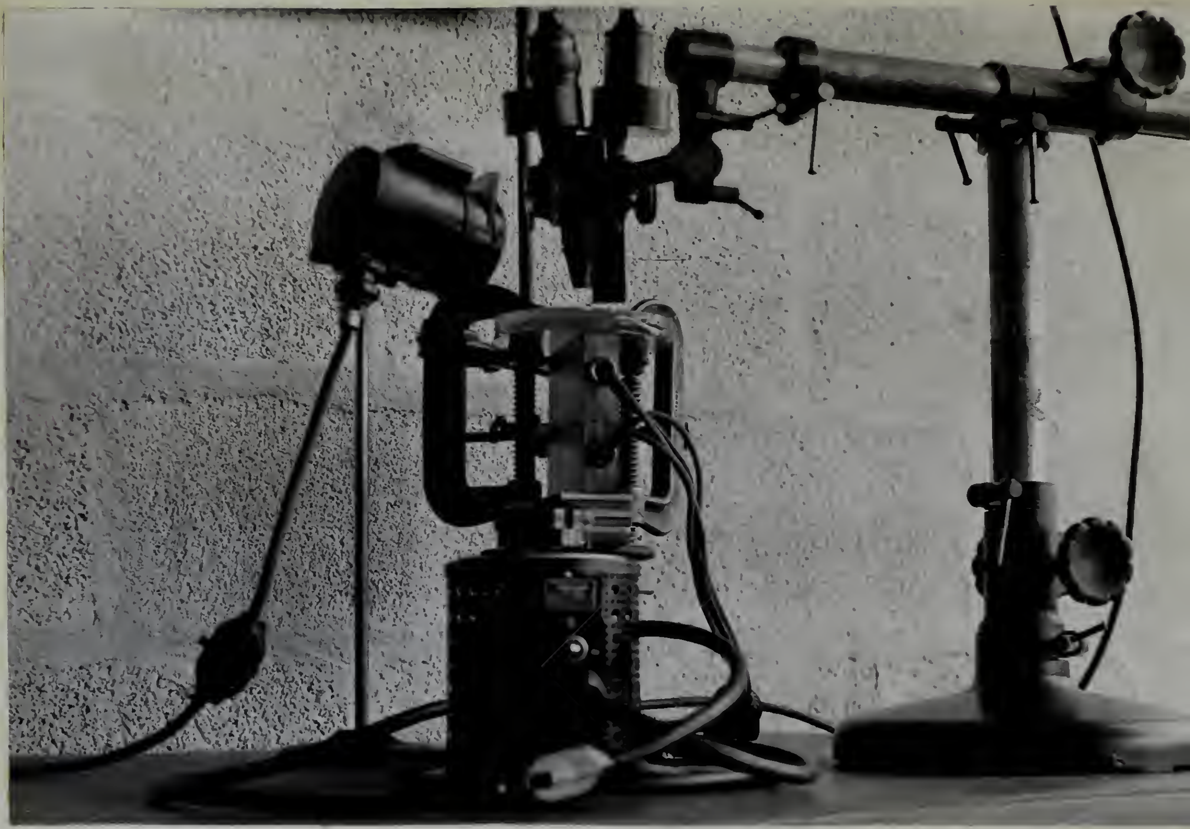
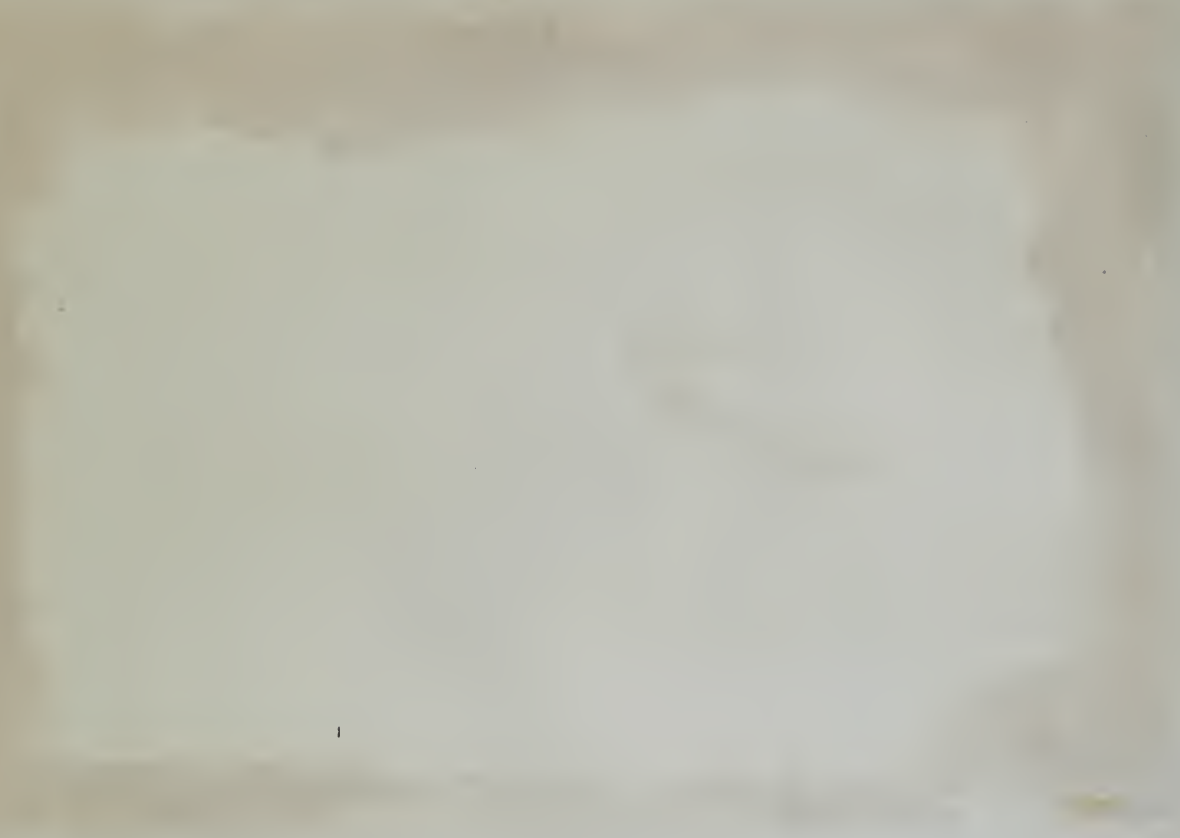


FIGURE 5

Apparatus used for Curing and Pressure Studies.



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TENSILE TESTING

Testing was accomplished in a Southwark 50,000 pound universal tester having an accuracy of ± 10 pounds. The disc specimens were one square inch in contact area, and self-aligning tension jigs were used to insure axial loading. After failure, the break was inspected visually and microscopically. The criterion of test acceptance was a failure partially or entirely in the adhesive. During the tests, not a single properly cured, clean specimen gave failure entirely at the metal interface.

While tensile testing does not evaluate all of the properties of the adhesive, it does give as good an evaluation as any other single test method, and previous investigators have used it more frequently than any other method.

EXPERIMENTAL DATA

Liquid Metal-to-Metal Adhesives: (40, 42, 43, 44)

Almost all metal adhesives are made by the addition of one or more of the thermosetting resins to one of the rubber resins. This adds strength and hardness to the bond since the thermosetting adhesives produce the strongest and most resistant bonds of all the various types of adhesives (38).

Textolite - is a rubber base phenolic resin adhesive manufactured by General Electric Company. It is a partially polymerized liquid of medium viscosity. It is a good metal-to-metal adhesive, but has a limited shelf life.

The specimens are dipped in the "Textolite", drained, and then dried for 18 hours in a vacuum desiccator after which they are assembled and cured in a heated press for fifteen minutes at 300 psi. In addition to the standardization runs, a total of 76 specimens were run using "Textolite". The data are in tables 1-6, inclusive. Humidity was not controlled except for the data in tables 1, 2, and 3.

Table 1

Adhesive	"Textolite"
Surface Cleaning	acetone
Cure Temperature	165°C
Cure Pressure	300 psi
Cure Time	15 minutes
Type of Metal	mild steel

Tensile Strength

Mechanical Surface Treatment:	1 Polished	2 Abraded	3 As Received
	2200 psi	2420 psi	2580 psi
	2280	2570	2300
	2520	2540	2630
	2600	2690	2450
Column Average:	2400	2555	2490

Analysis of variance (20). Slide rule accuracy.

$$\text{Total} = A + B = \sum_{0}^{k} \sum_{0}^{n} (xi)^2 - \frac{(\sum_{0}^{k} \sum_{0}^{n} xi)^2}{KN} = R - P$$

$$A = \frac{\sum_{0}^{k} (\sum_{0}^{n} xi)^2_n}{N} - \frac{(\sum_{0}^{k} \sum_{0}^{n} xi)^2}{KN} = S - P$$

B = Total - A (See appendix page 72)

Dividing xi in Table 1 by 10 and subtracting 242 gives:

xi_1^2	xi_1	xi_2^2	xi_2	xi_3^2	xi_3
484	-22	0	0	256	16
196	-14	225	15	144	-12
100	10	144	12	441	21
324	18	729	27	9	3

$\sum_0^n xi =$ -8 54 28

$(\sum_0^n xi)^2 =$ 1104 1098 850

$$\begin{array}{r} 1104 \\ 1098 \\ \underline{850} \end{array} \qquad \frac{(\sum_0^k \sum_0^n xi)^2}{NK} = \frac{5476}{12} = 456 = P$$

$$\begin{array}{r} 3050 \\ \underline{456} \\ 2596 \end{array} \begin{array}{l} = \sum_0^k \sum_0^n (xi)^2 \\ \\ = \text{Total} \end{array} \qquad R; \ \frac{\sum_0^k (\sum_0^n xi)^2}{N} = \frac{3764}{4} = 941 = S$$

Source of variation	Variation or sum of squared deviation	Degrees of freedom	Variance
Between columns - A	485	K - 1 2	243
Between rows - B	2111	K(N - 1) 9	235
Total	2596	(KN) - 1 11	---

$F = \frac{243}{235} = 1.034$

F for 5% tables = 4.26

No significant variation.

It is seen from the analysis of variance on Table 1 that there is no significant variation between the several conditions of surface preparation. As long as the surface is clean the mechanical surface treatment does not appear to be important. This does not apply to poorly fitted surfaces or to surfaces abraded to the extent that there are points of contact between the projections of two surfaces that are capable of stress concentrations.

An attempt was made to study the effect of sublimed metal films on the strength of bond. However, the failure occurred in the bond between the surface and the sublimed metal film, and thus the results were meaningless.

TABLE 2

Adhesive	"Textolite"
Surface Cleaning	Acetone
Cure Temperature	165°C
Cure Pressure	300 psi
Cure Time	15 minutes
Type of Metal	17 ST Aluminum

TENSILE STRENGTH

Mechanical Surface Treatment	1 Polished	2 Abraded	3 Mill Finish
	3030 psi	2430 psi	2450 psi
	2640	2410	2400
	2340	2770	2340
	2680	2550	2500
Column Average:	2672	2540	2422

Analysis of variance for table 2 is on page 74 in the appendix. There is no significant variation.

TABLE 3

Adhesive	"Textolite"
Surface Cleaning	Acetone
Cure Temperature	165°C
Cure Pressure	300 psi
Cure Time	15 minutes
Type of Metal	3 S Aluminum

TENSILE STRENGTH

Mechanical Surface Treatment:	1 Polished	2 Mill Finish
	1740 psi	1830 psi
	1920	1910
	1830	1860
	1780	1820
Column Average:	1818	1855

There is no significant variation between polished and mill finished specimens.

Despite the difference in the column means of tables 1, 2, and 3, analysis of variance indicates that there is no significant variation with mechanical surface treatment as long as the surface is chemically clean and free from dirt. This is contrary to the popular belief that abraded or sanded metals offer the best bonding surfaces. This misconception probably originated from the practice of sanding or abrading the surface in order to clean it, and instructions to sand the metal surface are not invalid as long as there is to be no chemical cleaning. However, for many applications a chemical cleaning is faster, more economical and should be employed.

This has recently been subatantuated by Moser (34) working with glass specimens. This despite the fact that metal surfaces are crystalline in nature and glass is non-crystalline.

TABLE 4

Adhesive	"Textolite"
Surface Cleaning	Acetone
Cure Temperature	165°C
Cure Pressure	300 psi
Cure Time	15 minutes
Mechanical Treatment	mill finish

TENSILE STRENGTH

Type of Metal:	Mild Steel	17 ST Aluminum	2 S Aluminum *
	2500 psi	2450 psi	1820 psi
	2300	2400	1910
	2430	2340	1880
	2400	2500	1800
Column Average:	2400	2422	1852

* Microscopic examination revealed the presence of metal slivers and oxide particles in the failed adhesive. The specimens appeared to have a heavy oxide coating.

It is believed that the significant difference observed in table 4, when the 2 S Aluminum data are included, was the result of poor wettability. The water break test was used as the criterion of cleanliness. It is possible that something in the history of the specimens resulted in good water wettability, but low adhesive wettability.

These specimens, after failure, were discarded and new specimens recently milled were used for the test data in table 8 which did not show a significant difference by the T test.

The results of table 4 are inconclusive, and the collection of more data is indicated. However, the results of the standardization tests indicate that most adhesives have a greater affinity for one metal than for another, even though there is normally no significant variation for the three metals tested on a 5-per cent level. For applications requiring maximum strength, use must be made of a specific adhesive properly selected.

CHEMICAL CLEANING

The methods of cleaning are self-explanatory, except for the special treatment. This special treatment consisted of immersing the parts in the cleaning bath, maintained at a temperature of 160 degrees F. for a period of five minutes. The composition of the cleaning bath was as follows:

Sodium Metasilicate (Anhydrous)	3.6 ounces
Alkyl Aryl Sodium Sulphonate	0.4 ounces
Tap Water	1.0 gallon

Immediately after removing from the cleaning bath, the parts were rinsed in running water and the surfaces examined for dis-continuity of the water film. If the water film was discontinuous, the parts were again immersed in the cleaning bath, as specified above, and rinsed. The cleaning and rinsing was repeated until the water film maintained its continuity.

The parts were then immersed in the chromic acid bath, maintained at a temperature of 140 to 160 degrees F. for a period of three minutes. The composition of the chromic acid bath was as follows:

Chromic Acid	5 per cent by weight
Tap Water	95 per cent by weight

After removing from the chromic acid bath, the parts were rinsed in distilled water and dried.

TABLE 5

Adhesive	"Textolite"
Cure Temperature	165°C
Cure Pressure	300 psi
Cure Time	15 minutes
Mechanical Finish	mill finish
Type of Metal	mild steel

TENSILE STRENGTH

Chemical Surface Treatment:	1 Electrolytic Etch	2 Solvent Degrease	3 2% Phosphoric Acid	4 Special Treatment
	2650 psi	2520 psi	2590 psi	2410 psi
	2330	2630	2810	2380
	2550	2470	2640	2560
	2750	2310	2760	2610
Column Average:	2570	2482	2700	2490

	5 Untreated Uncleaned
	2200 psi
	1410
	1450
	2420
Column Average:	1870

TABLE 6

Adhesive	"Textolite"
Cure Temperature	165°C
Cure Pressure	300 psi
Cure Time	15 minutes
Mechanical Finish	mill finish
Type of Metal	17 ST aluminum

TENSILE STRENGTH

Chemical Surface Treatment:	1 Solvent Degrease	2 2% Phosphoric Acid	3 Special Treatment	4 Untreated Uncleaned
	2450 psi	2610 psi	2760 psi	2210 psi
	2410	2570	2590	1430
	2330	2380	2470	1180
	2500	2460	2410	1940
Column Average:	2422	2507	2558	1690

Analysis of tables 5 and 6 indicate quite conclusively that there is no significant variation between the methods of chemical cleaning that were tested. However, there is a significant difference in tensile strength between clean and unclean specimens. This indicated that the most economical method of chemical cleaning should normally be used.

REDUX

The third adhesive investigated has the trade name "Redux", and is a liquid thermosetting resin designed for bonding metal-to-metal and metal-to-wood. This is a phenolic $-CH_2O$ base adhesive with a vinyl resin added. It requires the use of an acid catalyst in the form of a stable, white granular powder manufactured by the Resinous Products and Chemical Company. One of the greatest limitations is its storage properties. The liquid Redux must be refrigerated, and has a maximum storage life of about two months.

The data for Redux are in tables 7-9 inclusive.

TABLE 7

Adhesive	Liquid Redux with catalyst
Cure Temperature	149°C
Cure Pressure	300 psi
Cure Time	15 minutes
Mechanical Finish	mill finish
Cleaning Agent	acetone

TENSILE STRENGTH

	1	2
Type of metal:	Mild Steel	17 ST Aluminum
	3900 psi	4070 psi
	3810	4300
	4540	4300
	4080	4810
Column Average:	4083	4370

No significant variation by the two-tail T test.

ADHESIVE FILMS

One of the major problems in the use of adhesives is in their application. When using liquid adhesive, it is difficult to obtain uniform dependable results, even with experienced personnel. The lengthy time of drying and precure prevents the use of adhesives in many metal-to-metal bonding applications. The elimination of these two operations would extend adhesive bonding to many more applications.

The industrial implications of using adhesive films in preference to liquid adhesives are numerous. The use of films, where applicable, will reduce wastage, eliminate messy handling, allow wider use of unskilled labor, eliminate holdup-time resulting from the precure and pre-drying operations, and insure more uniform and more dependable results.

In this phase of the work the impregnation of various papers and textiles with adhesives were investigated (25). Most of the textile fabrics proved unsatisfactory because the fibers either supported too much adhesive or gave uneven, irregular impregnation. The papers tested were filter paper, lens paper, cellulose wadding, tissue paper, glassine paper, and special plastic papers (18, 38, 47). The most successful ap-

plications were with uncalendered tissue paper having chemically pure cellulose fibers. Even then trouble was experienced with adhesives having a low PH because of the acid attack on the cellulose. After considerable investigation and studies, tissue paper was satisfactorily impregnated with Redux, Cycleweld, and Pliobond. These experimental impregnated films were tested, and the results compared with an industrial experimental film that is now in pilot plant production. This film is "Permacel #1525", manufactured by the Industrial Tape Corporation. After studying the properties of these films, it was concluded that films properly selected could be used for most industrial applications. However, not all adhesives lend themselves to the formation of impregnated films. Under such circumstances it should be possible to use dried films of the adhesive as in "Permacel 1525". However, these films, unless extremely thin, are more brittle than impregnated films. The results of tests using experimental films are in tables 8, 9, 10, and 11.

REDUX EXPERIMENTAL FILM

The experimental film was made by submerging sheets of thin tissue paper in a container of medium viscosity Redux for two hours, removing, draining, and resubmerging for a similar period. This was followed by a one hour period for draining and drying before cutting the film to size and making the assemblies for curing. This process gave a final cured glue line of approximately three mils thickness when one layer of film was used.

TABLE 8

Adhesive	Experimental "Redux" film
Cure Temperature	150°C
Cure Pressure	300 psi
Cure Time	15 minutes
Mechanical Finish	mill finish
Cleaning Agent	acetone
Thickness of Film	one layer

TENSILE STRENGTH

Type of metal:	1 2 S Aluminum	2 17 ST Aluminum
	2200 psi	2710 psi
	2410	2640
	2380	2430
	2350	2590
Column average:	2335	2592

TABLE 9

Adhesive	Experimental "Redux" Film
Cure Temperature	340°F
Cure Pressure	300 psi
Cure Time	15 minutes
Mechanical Finish	mill finish
Cleaning Agent	acetone
Type of Metal	17 ST aluminum

TENSILE STRENGTH

Film Thickness:	1 2 layers*	2 2 layers** After 3 months storage	3 1 layer* After 3 months storage
	2540	1980	2340
	2660	2310	2330
	2810	2430	2280
	2540	2370	2450
Column Average:	2625	2298	2350

* Specimens were prepared and tested as soon as the impregnated carrier films were made and dried.

** Specimens prepared 3 months after the film was made and stored.

PLIBOND

Plibond is a viscous, tan colored thermoplastic adhesive manufactured by the Goodyear Tire and Rubber Company. This is a rubber base adhesive having 30 per cent solids in a solution of methyl ethyl ketone. This thermoplastic adhesive was used to give an indication as to how thermoplastic adhesives compare with thermosetting adhesives; the data are in table 10.

CYCLEWELD

Two types of Cycleweld manufactured by the Chrysler Corporation were used in the film formation. The C-3 Cycleweld is a mixture of phenol formaldehyde, carbon black, rubber and solvents (36, 37). As seen from the data in table 10 this adhesives does not lend itself well to use as impregnated films. The 55-9 Cycleweld which is also a phenolic rubber base adhesive gave more encouraging results when used as an impregnated film than did the C-3 Cycleweld.

TABLE 10

Cure Temperature	330°F
Cure Pressure	300 psi
Cure Time	15 minutes
Mechanical Finish	ground surface
Type of Metal	mild steel
Cleaning Agent	acetone

TENSILE STRENGTH

Type of Adhesive:	Liquid Cycleweld 55-9	Film Cycleweld 55-9	Film Cycleweld 55-9 After 3 months storag
	2710 psi	2440 psi	2050 psi
	2640	1860	1960
	2820	1640	1890
	2760	2300	1860
Column Average:	2732	2060	1940

	Liquid Cycleweld C-3	Film Cycleweld C-3	Liquid Pliobond	Film Pliobond
	2440 psi	820 psi	1840 psi	1880 psi
	2700	500	1910	1810
	2660	250	2070	1660
	2740	480	1730	1720
Column Average:	2636	512	1888	1768

The data for impregnated tissue paper films are presented in tables 8, 9, and 10. The reduction in tensile strength when using carrier film adhesives, as compared to the same adhesives in liquid form, are:

Type of adhesive	Per cent reduction in strength
Cycleweld 55-9	24
Cycleweld C-3	81
Pliobond	6
Redux	40

However, in all cases except Cycleweld C-3, the impregnated film gave good enough strength for normal applications and development work should result in better strength properties for these films. Some adhesives, such as Cycleweld C-3, are not well adapted to use as impregnated tissue paper films, and under such circumstances dry films of the adhesive similar to Permacel 1525 can usually be made.

Some papers could not be impregnated because they disintegrated upon contact with the adhesive.

TABLE 11

Adhesive	"Permacel #1535" Polyvinyl Butyral Phenolic Film*
Cure Temperature	150°C
Cure Pressure	200 psi
Cure Time	15 minutes
Mechanical Finish	mill finish
Type of Metal	mild steel
Thickness of One Layer of Film	three mils
Cleaning Agent	acetone (except for columns 2 and 3)

TENSILE STRENGTH

	1 One Layer** (dri-film)	2 One Layer (flame clean)	3 One Layer (unclean)
	3700 psi	3980 psi	1100 psi
	4100	4110	1310
	3550	4060	1380
	3920	4320	1580
Column Average:	3818	4118	1342

TABLE 11 (continued)

	4 One Layer (4 months old)	5 One Layer (unaltered)	6 Two Layers
	3810 psi	3920 psi	3840 psi
	3960	3880	4310
	3710	4620	4060
	3530	4200	3920
Column Average:	3752	4155	4032

	7 Three Layers	8 Four Layers
	3700 psi	3120 psi
	3680	3060
	3850	3300
	3520	3240
Column Average:	3688	3180

*Experimental Film - pilot plant material not yet in production.

**Coated with General Electric's organo-silicon water repellent film number 9877-2.

From the data in tables 5, 6, and 11 it would appear that cleanliness is a more important variable in film bonding than it is in liquid bonding. This may be because the liquid results in a washing action on the surface.

A plausible explanation for the high results obtained with "dri-film" in table 11 is a chemical attachment of the adhesive to the organosilicon film despite the reduction in wettability of the metal surface by the "dri-film". This is apparently the result of affinity of the adhesive for the polar molecules of the silicon film. Also of importance is the fact that while "dri-film" appreciably reduces the water wettability, it reduces the adhesive and solvent wettability to a much lesser extent. This emphasizes a point that is apparently not realized in industry. The point is that a better criterion of surface conditioning would be the degree of solvent and adhesive wettability rather than the water wettability (16). This is driven home by the fact that the water break test and the contact angle test both indicate that the organosilicon film is a poor bonding surface, yet it gives excellent results.

From table 11 the reduction in strength of Fermacel 1535 after four months storage was about 10 per cent. This was found despite the lack of special stor-

age facilities. Table 11 also shows that increasing the film thickness reduces the bond strength. This is illustrated graphically on page 61, and confirms the results of previous investigations (15, 29).

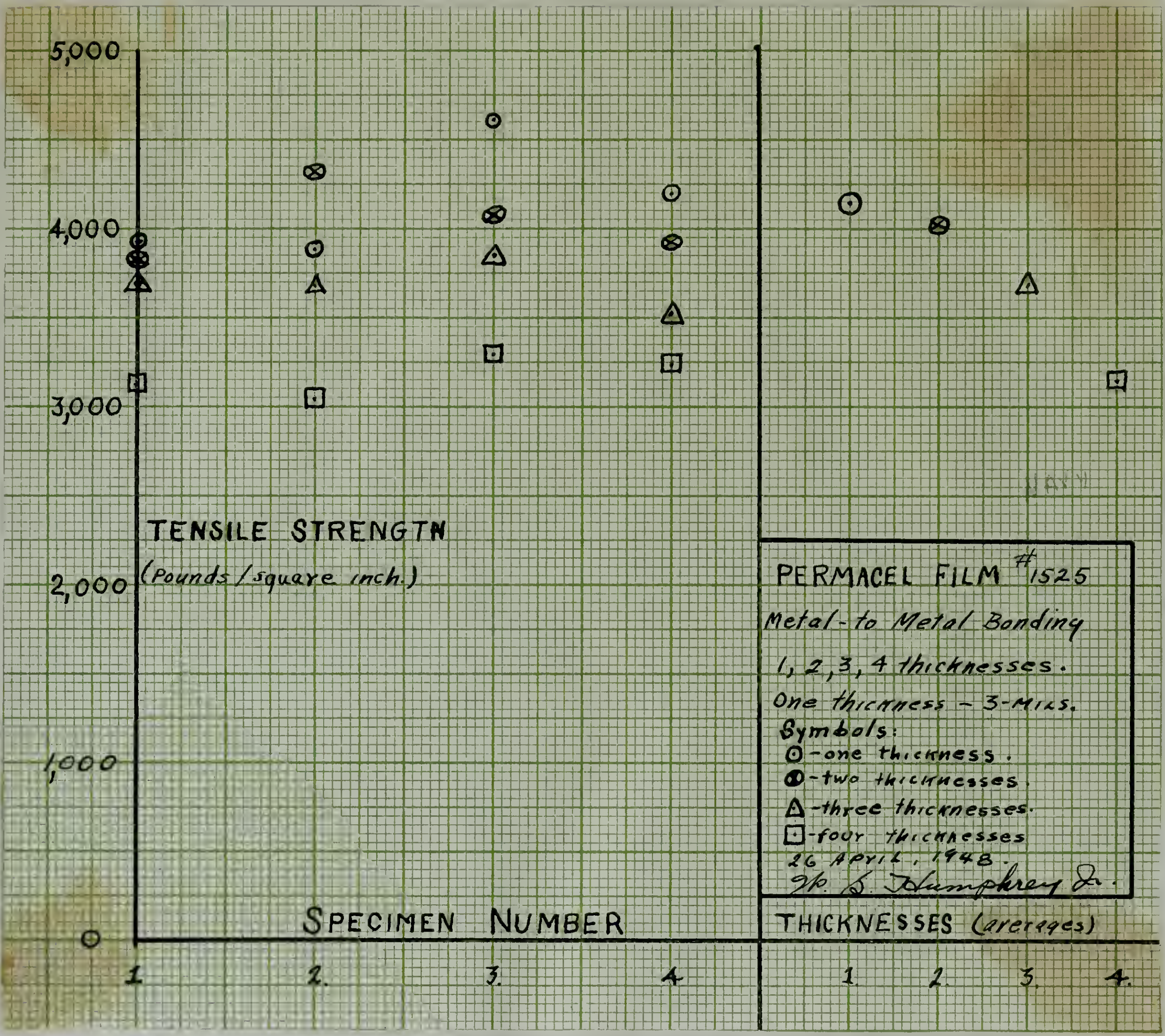
For the flame cleaning a blast lamp with an oxygen, natural gas flame was used. This offers a rapid, economical method of degreasing and removing the adsorbed surface film where the change in physical properties of the metal, brought about by the heating are not objectionable. This is a new method of cleaning for adhesive bonding and a literature survey failed to reveal any previous investigation along these lines. The method compares well with chemical cleaning as seen from table 11 and has many industrial implications.

Strength After Storage:

From tables 8, 9, 10, and 11 the per cent reduction in tensile strength after storage are:

Metal-to-metal adhesive	Length of storage	Per cent reduction in strength
Redux	3 months	9.5
Cycleweld 55-9	3 months	5.8
Permacel 1525	4 months	10.

The storage was in an inside cabinet during the winter months when the humidity was low and the temperature seldom more than 18°C.



Correlation of Tensile Strength and Film Thickness.

Considerably more data were collected during the experimental work, some 500 specimens being tested in all. Only data having direct bearing on the results are included in this presentation.

SUMMARY

It is recognized that surface properties have a direct bearing on the strength of adhesion. However, adherence to a chemically clean surface appears to be more a function of the relationship between the active groups on the molecules of the adhesive and the surface being bonded, than a function of mechanical surface treatment. This can only be verified by the successive elemination and evaluation of mechanical variables by methods that present techniques are unable to analyze. The fact that most molecularly associated substances contain hydroxyl or related groups leads to the conclusion that this type of bond may play an important part in the role of cohesive and adhesive phenomena and will differ from metal to metal. Tensile testing and analysis of variance were used to measure the significance of the variables studied at the 5 per cent probability level. The humidity was controlled only on the first three tests. Ten industrial adhesives developed during or since World War II were studied, six of which are reported in the data. The preparation and use of impregnated films was also studied. Of the impregnated films tested, ordinary uncalendered tissue paper gave the best results. All test data presented on the use of impregnated papers in adhesive applications were with tissue

paper as the carrier film.

The precure must be such that polymerization is not extensive. High degrees of polymerization, before assembly, result in loss of strength at the adhesive-adhesive interface when the assembly is made.

Rapid drying results in blisters and cracks. The thicker the film the slower the dry must be; the optimum is a film just sufficiently thick to prevent a starved joint.

Pressure during the cure operation serves the following functions:

1. Proper flow of adhesive.
2. Holds the mating surfaces in proper position.
3. Reduces the void space in the adhesive.
4. Insures even pressure distribution.

Degassing of the adhesive followed by flowing it between the mating surfaces by capillary action results in a non-porous joint.

This investigation indicates that (1) There is no significant variation between the bonding properties of the normal types of chemical and mechanical surface treatments as long as the surface is chemically clean and free from dirt and grease. (2) A specific adhesive displays a greater affinity for one type of metal than for another, depending upon its composition. (3) Adhesive films and impregnated tapes can be pre-

pared and employed advantageously in industrial applications. (4) Flame cleaning may be used to satisfactorily clean metal surfaces prior to bonding in applications where changes in the properties of the metal with heating are not objectionable. This is a new approach to surface cleaning and has industrial possibilities. (5) Bond strength diminishes as film thickness increases. (6) The criterion of cleanliness should be adhesive and solvent wettability not water wettability.

The reduction in tensile strength when using carrier film adhesives as compared to the same adhesive in the liquid form:

Type of Adhesive	Per cent reduction in strength
Pliobond	6
Cycleweld 55-9	24
Redux	40
Cycleweld C-3	81

The reductions in strength of the films after storage are:

Type of Adhesive	Length of Storage	Per cent reduction in strength
Cycleweld 55-9	3 months	5.8
Redux	3 months	9.5
Permacel 1525	4 months	10.0

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APPENDIX

Analysis of variance offers solutions for two kinds of problems:

1. Detection and estimation of constant relations among the means of sub-groups of the population of objects concerned. In other words, it is used to detect and estimate the parameters defining fixed constant relations among the population means.
2. Detection and estimation of components of variation associated with a composite population; that is, it can be used to estimate the components of variance.

The general purposes of analysis of variance are:

1. To perform tests of significance.
2. To peform estimates of treatment differences that are of concern.
3. To determine the accuracy of estimates by attaching to them confidence limits.

The assumptions involved in making an analysis of variance are:

1. The treatment and environmental effects must be additive.
2. The experimental errors must all be independent.
3. The experimental errors must be normally distributed.

Many investigators have pointed out that no serious errors are normally introduced by non-normality in the significant levels of the F or two-tailed T test (8, 20). In this investigation the 5 per cent probability level is used throughout.

This work demonstrates the general applicability of statistical analysis to problems in chemical testing. The limitation of time for testing was such that it was necessary to use statistical analysis on the data. A single application of the analysis of variance is well adapted to the particular problem. Graphical analysis would have required the running of a much greater number of samples. The analysis of variance was selected as the means of presenting the data because it provides a basis for analyzing a number of variables simultaneously. The problem as analyzed is a series of samples taken under varying conditions. The use of variance analysis is contingent upon the samples being from a normal distribution.

The analysis of variance is set up for K conditions with N random specimens for each of the K conditions. The variables were randomized by giving each of the samples of the experiment an equal opportunity of having any particular value of the randomized variable associated with it. The variance is:

$$s^2 = \frac{\sum_{0}^{K}\sum_{0}^{N}(Xi - \bar{\bar{X}})^2}{N(K-1)}$$

Rearranging and expanding where $Xk = \bar{X}k$ = column mean.

$$\sum_0^K \sum_0^N (Xi - \bar{\bar{X}})^2 = \sum_0^K \sum_0^N \left((Xi - Xk) + (Xk - \bar{\bar{X}}) \right)^2$$

$$= \sum_0^K \sum_0^N (Xi - Xk)^2 + (Xk - \bar{\bar{X}})^2 + 2 \text{ cross product}$$

$$\sum_0^N 2 \text{ cross product} = 2 \sum_0^N Xi\ Xk - Xi\ \bar{\bar{X}} - Xk^2 + Xk\ \bar{\bar{X}}$$

$$= 2\ \bar{X}k \sum_0^N Xi - 2\ \bar{\bar{X}} \sum_0^N Xi - 2\ N\bar{X}k + 2\ \bar{\bar{X}}N\bar{X}k$$

$$= 2\ \bar{X}k \sum_0^N Xi - 2\ X \sum_0^N Xi - 2\ N\bar{X}k \sum_0^N \frac{Xi}{N} + 2\ \bar{\bar{X}} \sum_0^N \frac{XiN}{N}$$

$$= 0$$

Thus

$$\sum_0^K \sum_0^N (Xi - \bar{\bar{X}})^2 = \sum_0^K \sum_0^N (Xi - Xk)^2 + (Xk - \bar{\bar{X}})^2$$

$$= \sum_0^K \sum_0^N (Xi - \bar{X}k)^2 + \sum_0^K \sum_0^N (\bar{X}k - \bar{\bar{X}})^2$$

$$= \sum_0^K \sum_0^N (Xi - \bar{X}k)^2 + \sum_0^K N\ (\bar{X}k - \bar{\bar{X}})^2\ .*$$

---

* Since $\bar{X}$ for each column is constant through N for each K condition. First sum through K and then through the N's.

$$\text{Total variance} = \sum_{0}^{K}\sum_{0}^{N}(Xi)^2 - \frac{(\sum_{0}^{K}\sum_{0}^{N}Xi)^2}{KN} = R - P.$$

$$= A + B$$

where A = variance between columns,

B = variance within columns

B = total variance - A

$$A = N\sum_{0}^{K}(\bar{X}k - \bar{\bar{X}})^2 = \sum_{0}^{K}\frac{(\sum_{0}^{N}Xi)^2}{N} - \frac{(\sum_{0}^{K}\sum_{0}^{N}Xi)^2}{KN},$$

$$= S - P.$$

F test = A/B

$$\bar{X}k = Xk = \text{column mean} = \sum_{0}^{N}\frac{Xi}{N}$$

It is constant as we sum through N.

For application of this to the data see page 74.

SAMPLE CALCULATIONS

Dividing Xi in Table 2 by 10 and subtracting 250 gives:

	Xi_1^2	Xi_1	Xi_2^2	Xi_2	Xi_3^2	Xi_3
	2809	53	49	-7	25	-5
	196	14	81	-9	100	-10
	256	-16	729	27	256	-16
	324	18	25	5	0	0
$\sum_0^N Xi =$		69		16		-31
$\sum_0^N Xi)^2 =$	3585		884		381	

3585
884
381

$4850 = \sum_0^K \sum_0^N (Xi)^2 = R$

-243

4607 = Total

-1251

3356 = B

$$\frac{(\sum_0^K \sum_0^N Xi)^2}{NK} = P = 243$$

$$\frac{\sum_0^K (\sum_0^N Xi)_N^2}{N} = S = 1494$$

-243

A = 1251

Source of Variation	Variation or Sum of Squared Deviation	Degrees of Freedom	Variance
A	1251	2	626
B	3356	9	373
Total	4607	11	---

F - 5% Tables = 4.26

$$F = \frac{626}{373} = 1.68$$

No significant variation.

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